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13. ABSTRACT (Maximum 200 words) On the theoretical side, a new highly scalable code for frozen core second order perturbation theory gradients for closed shell molecules has been developed. The development of analogous codes for molecules with unpaired electrons is in progress. A sequential unrestricted code for this purpose has been completed. The derivation for the spin-restricted open shell second order perturbation theory gradients has been completed, and a paper describing this derivation has now been accepted. Other important developments are new convergence methods for MCSCF wavefunctions that facilitate MCSCF calculations on large molecules, the derivation of gradients for multi-reference second order perturbation theory, the development and implementation of a full-CI method that is amenable to parallelization, further developments of our effective fragment potential (EFP) method for studying solvation and liquid behavior, the development of molecular dynamics and Monte Carlo methods to facilitate the study of solvation and liquid behavior, the development and implementation of a new method for producing global potential energy surfaces from sets of ab initio points, the development and implementation of both grid-based and gridless approaches to density functional theory, and the development and implementation of several MjCSCF-based approaches to spin-orbit coupling. With regard to applications, considerable progress has been made in our understanding of the mechanisms for formation of POSS (polyhedral oligomeric silsesquioxanes) and the possibility of passing small gas molecules through them. POSS titanium analogs have also been studied, as have the hydrosilation and bis-silylation reactions. Other applications include studies of surface chemistry, several silicon systems and studies of the behavior of water clusters.			
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1. COVER SHEET

AFOSR FINAL REPORT

THEORETICAL STUDIES OF SILICON AND RELATED ELEMENTS

AFOSR F49620-98-1-0164

11/1/98 – 10/31/01

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2. Objectives: No Change in Objectives

3. Status of effort: A brief statement of progress towards achieving the research objectives. (Limit to 200 words.)

On the theoretical side, a new highly scalable code for frozen core second order perturbation theory gradients for closed shell molecules has been developed. The development of analogous codes for molecules with unpaired electrons is in progress. A sequential unrestricted code for this purpose has been completed. The derivation for the spin-restricted open shell second order perturbation theory gradients has been completed, and a paper describing this derivation has now been accepted. Other important developments are new convergence methods for MCSCF wavefunctions that facilitate MCSCF calculations on large molecules, the derivation of gradients for multi-reference second order perturbation theory, the development and implementation of a full-CI method that is amenable to parallelization, further developments of our effective fragment potential (EFP) method for studying solvation and liquid behavior, the development of molecular dynamics and Monte Carlo methods to facilitate the study of solvation and liquid behavior, the development and implementation of a new method for producing global potential energy surfaces from sets of *ab initio* points, the development and implementation of both grid-based and gridless approaches to density functional theory, and the development and implementation of several MCSCF-based approaches to spin-orbit coupling. With regard to applications, considerable progress has been made in our understanding of the mechanisms for formation of POSS (polyhedral oligomeric silsesquioxanes) and the possibility of passing small gas molecules through them. POSS titanium analogs have also been studied, as have the hydrosilation and bis-silylation reactions. Other applications include studies of surface chemistry, several silicon systems and studies of the behavior of water clusters.

4. Accomplishments/New Findings: Describe research highlights, their significance to the field, their relationship to the original goals, their relevance to the AF's mission, and their potential applications to AF and civilian technology challenges.

A. THEORY/MODEL DEVELOPMENT

Parallel Developments. A highly scalable code for frozen core second order perturbation theory gradients for closed shell molecules has been developed and is on-line for general use at several IBM SP2 and Cray T3E systems, including the T3Es at ERDC and NAVO and the SP2 at Maui. This new code uses the Distributed Data Interface (DDI) so that the large arrays do not have to be replicated. This means that much larger molecules can be studied using geometries based on correlated wavefunctions. The code scales very well for as many as 512 nodes and has already been applied to several challenging compounds. The development of analogous codes for molecules with unpaired electrons, using both restricted and unrestricted wavefunctions, is in progress. A sequential unrestricted MP2 code has been completed. A paper on the restricted open-shell

derivation has been accepted. A paper on a DDI implementation of the SCF method has been published. Improved parallel MCSCF codes are under development, and an initial parallel full CI code has been implemented. The multi-reference perturbation theory code (MCQDPT) has now been implemented under DDI. Part of the effective fragment potential (EFP) code has been made scalable, and the remainder of the code will be addressed in the coming year. In an important related development, parallel GAMESS now runs on clusters of PCs and Macs (running Linux) and high end workstations. This is more challenging than self-contained massively parallel computers, since the overhead due to inter-node communications is more complex. This issue has been solved to some extent by using a Gigabit Ethernet switch with large data packets. We are also exploring alternative communications solutions, such as Myrinet and SCI. These developments will be enhanced by the construction of a new 32-node, 128-CPU IBM Power3+ cluster using funds provided by a DURIP grant. As for all other GAMESS developments, we will make our experiences in developing scalable clusters available to all users.

Condensed Phase Methods. We have already shown that our effective fragment potential (EFP) method for solvation is excellent for water, in a variety of applications. We are now working on extending the capabilities of the method in several ways. We are exploring several alternative approaches for incorporating dispersion and other higher order terms into the method. Such terms are particularly important for nonpolar solvents. We are also in the process of extending the model so that it is equally applicable and accurate for any solvent. Key to the success will be the derivation of general expressions for charge transfer and dispersion contributions that contain no fitted parameters. The derivation of an expression for the analytic gradient for the EFP-*ab initio* interaction term is in progress. A very important new development (by co-worker Jan Jensen) is a new method for using EFPs across covalent bonds. This will facilitate the representation of large substituents, as well as the treatment of large biological molecules. We have also interfaced the EFP method with two continuum methods, the simple Onsager reaction field and the more sophisticated polarizable continuum model (PCM).

As the number of solvent molecules in the system increases, the number of configurations to be considered increases rapidly, and traditional small molecule geometry optimization methods are not effective. We are therefore developing both molecular dynamics and Monte Carlo simulation codes so that the configurational space can be probed more effectively, not only for minima, but for transition states and reaction paths as well. This is also an important first step in the development of methods based on the EFP model for predicting bulk properties and super-critical behavior. We are therefore incorporating Ewald summations into our MD method. Collaborators in this effort are Dr. Paul Day (AFRL) and Professors Teresa Head-Gordon (UC-Berkeley) and Grant Merrill (University of Missouri). Related to these dynamical methods is our development and implementation of a method for converting the large numbers of points generated in *ab initio* trajectories into a global potential energy surface, using a modified Shepard interpolation approach.

Major James Shoemaker's Ph.D dissertation in Engineering Physics at the Air Force Institute of Technology focused on the development and applications of an embedded

cluster model for treating surface chemistry. A paper on the theoretical method, called SIMOMM, has been published in the Journal of Physical Chemistry. Several papers applying this method have now been published or submitted, and a manuscript that describes applications to silicon carbide surfaces is in progress. Extensions of this method to transition metal catalysts are planned; however, molecular mechanics is not likely to be a viable approach for the bulk, since electrons in such systems are too delocalized. To overcome this potential problem, we have begun to explore fast multipole methods (FMM) that scale linearly and are also highly parallel, so that the bulk part of the system can be treated by quantum mechanics. One preliminary paper has been published and the first FMM paper has been published as well.

Other developments There are many problems that involve species for which one cannot write one simple Lewis structure. Such species must be treated with multi-configurational (MCSCF) wavefunctions. However, the computational demands for MCSCF calculations are very high. So, we have developed a set of methods for converging such wavefunctions that range from very rapid convergence with high CPU and disk requirements to methods that converge more slowly but have very modest computational demands. The advantage of the latter is that much larger molecules than normal can be treated with this method.

For species that must be treated with MCSCF wavefunctions, non-traditional methods are also needed to recover the dynamic correlation. One method that has been implemented into GAMESS is multi-reference second order perturbation theory. The gradient formulas for this method have been derived, and the implementation into GAMESS is in progress. The key collaborator in this effort is Dr. Haruyuki Nakano (University of Tokyo).

There are many problems that involve multiple electronic states on multiple potential energy surfaces. Since such surfaces can cross and therefore induce radiationless transitions, it is important to have the capability to predict non-adiabatic coupling among these surfaces. One origin of non-adiabatic interactions among surfaces is spin-orbit coupling. Spin-orbit coupling matrix elements must be calculated using multi-reference wavefunctions, but until recently, there have been no generally available codes for the computation of these matrix elements using all electrons and any arbitrary MCSCF wavefunction for any arbitrary set of spin states. We have now developed and implemented such a method. It will be particularly valuable for the study of high energy density materials and for the study of any processes involving transition metals, since both types of species involve multiple electronic states. Since such all-electron calculations are very demanding, two alternative approaches to this problem have also been developed and implemented into GAMESS for use with larger molecules. One of these is called the Z_{eff} method, in which the two electron term is ignored and a fitted empirical parameter is introduced into the one-electron part of the Hamiltonian. While this is a very efficient approach, its accuracy is limited. However, there is an intermediate method, in which only those matrix elements connecting orbitals in the active space with each other are neglected. We have shown that in this case excellent agreement with the all electron method is obtained, without any need for fitted

parameters. We have also implemented the RESC (relativistic elimination of the small component) method for calculating spin-orbit coupling interactions, complete with analytic gradients.

Density functional theory (DFT) has become extraordinarily popular in recent years, because it has the same computational requirements as Hartree-Fock theory, but often has a level of accuracy that is comparable to second order perturbation theory. We have developed and implemented a gridless approach to DFT, by using the resolution of the identity to evaluate the complicated integrals. This procedure requires the use of auxiliary basis sets to resolve the identity. After extensive analysis of the convergence of several molecular properties as a function of basis set, we have recommended a series of auxiliary basis sets for use with the first row in the periodic table. The next step will be to extend this basis set development to heavier elements. We have also implemented a more traditional grid-based DFT method, including all of the most popular functionals.

Another approach that is very important for large molecules, especially molecules that contain heavier elements, is the effective core potential (ECP) method. This method replaces inner shell electrons by model potentials, making the calculations much more efficient. These potentials include relativistic corrections for the heavier elements. To make these calculations more useful, we have developed much more efficient methods for obtaining the first and second energy derivatives; that is, the gradients and Hessians. The increase in speed is a factor of 5-10, and the method has been implemented to take advantage of parallel computers.

As calculations on larger and larger species are made feasible by advances in parallel programs and other innovative algorithms, it becomes increasingly important to develop graphical methods for interpreting the results of complex calculations. This has led to the continuing development of MacMolPlt, a graphical interface for GAMESS. MacMolPlt provides the ability to visualize (and rotate in real time) orbitals, wavefunctions, electron densities and electrostatic potentials in two and three dimensions. We are now in the process of developing a Windows based version of this code.

We have also been exploring alternatives and extensions to the popular G2 and G3 methods developed by Pople and co-workers for the accurate prediction of such thermodynamic properties as heats of formation, ionization potentials and electron affinities. One limitation of these methods is that they are applicable only to species that are adequately described by single configuration wavefunctions. This eliminates many transition metal compounds, diradicals and most transition states. We have therefore initiated, in collaboration with the Radom group, the development of multi-reference analogs of the G2 and G3 methods. The multi-reference methods are based on CASSCF wavefunctions, instead of Hartree-Fock, followed by multi-reference perturbation theory (instead of MP2) and finally multi-reference CI. The initial paper describing this method has been published.

B. APPLICATIONS

POSS Compounds. Polyhedral oligomeric silsesquioxanes (POSS) have a wide variety of important applications, including lubricants and coatings. Consequently, there is considerable interest in these species in industry, universities and Air Force Laboratories. We have therefore initiated a detailed study of POSS compounds, with primary emphasis on the mechanisms by which these species form, in both the gas phase, and in solution and the presence of catalysts. In the first series of calculations, we examined the three stepwise hydrolysis steps of trichlorosilane, followed by the condensation of the product trihydroxysilane. All four reactions are predicted to have large barrier heights in the gas phase, but the addition of just one extra water molecule is sufficient to reduce all barriers to zero or nearly zero, except for the first hydrolysis step. In the latter, there is still a residual barrier of almost 10 kcal/mol. So, the next step will be to examine the effect of additional water molecules, especially on this first step. Since these are rather large species, the additional water molecules will be treated with the EFP method. The molecular dynamics (MD) and Monte Carlo (MC) codes, now almost completed, will be essential as the number of water molecules is increased.

For both the hydrolysis and condensation steps in the POSS mechanism, there exist low lying intermediates. Even though the net barriers are nearly all small in the presence of an additional water molecule, the barriers separating these intermediates from products are large. So, it is not entirely clear how easily products will be obtained in solvent. To determine this, *ab initio* dynamics "on-the-fly" will be carried out in the presence of waters, using the MD and MC codes.

Calculations have also been completed on the next steps in the mechanism, in which the initial condensation products, disiloxanes, are further condensed to the ring compounds D3 and D4. These results are consistent with those reported above, in that initially high barriers are reduced to nearly zero by an additional water molecule. The next steps in this process will include further condensation to the three-dimensional cages and analysis of substituent effects on the reaction mechanism and energetics.

Although our main focus is on Si-based POSS, the Ti analogs are also of interest. We have therefore initiated a series of calculations on the Ti-POSS compounds to study their properties. The first paper on mixed Si-Ti POSS has been published.

Three dimensional cage compounds, including zeolites, have been of interest as a possible means for separating small gas molecules. In collaboration with Dr. Shawn Phillips (AFRL-Edwards) we have therefore initiated a series of calculations in which the potential energy surfaces for passing N_2 and O_2 through the faces of T_n , $n = 8, 10, 12$. For T_8 , both the energy barriers and the endothermicities are very large for both N_2 and O_2 . In both cases, electron correlation is essential for an adequate estimate of the energetics. For N_2 , the barrier height is on the same order as the SiO bond strength, while the O_2 barrier is much smaller. Despite these observations, the SiO bond does not break upon entry of either molecule, and the species with the gas molecules are minima on their respective potential energy surfaces. As the size of the cages increases, the barriers and endothermicities decrease as one would expect.

Hydrosilation and Bis-silylation. The hydrosilation and bis-silylation reactions are among the most important means for producing new silicon-carbon bonds. We have shown that both of these reactions have very high barriers in the absence of a catalyst, so the catalyst clearly plays an essential role. We have now examined the role of the catalyst on the hydrosilation reaction in some detail, both for the prototypical reaction of silane + ethylene in the presence of model catalyst TiH_2 , and for more complex reactions of trichlorosilane with catalysts TiCl_2 and TiCp_2 , where Cp is cyclopentadienyl. The fundamental mechanism is the same in all cases: TiX_2 initially forms a very stable three-membered ring intermediate, with a very large drop in energy. This is followed by the formation of a weakly bound complex with the silane. Both of these steps are downhill with no intervening barrier. This energy release in all cases is sufficient to overcome the barriers in the two subsequent steps in the reaction. So, the basic role of the catalyst is to drive the energy far downhill via the formation of a strongly bound complex with one of the reactants. Similar studies are now underway for the bis-silylation reaction, using both TiX_2 and Pt-based catalysts. Related silicon chemistry includes the detailed study of the molecular and electronic structure of silicocene, the silicon analog of ferrocene, and the reactions of alkyl-substituted silylenes with several alkenes, in order to understand the kinetics of these reactions. The Cp rings in the silicocene molecule are very fluxional, so a very high level of theory is required for a reliable structural prediction. The parallel MP2 gradient code has been essential for this project. The silylene reaction calculations are in excellent agreement with experiment.

Water Clusters and Solvation. Recent papers by Wales and co-workers have made it clear that nearly all available model potentials fail to reproduce *ab initio* structures or energetics for small to medium size water clusters. We have therefore initiated a systematic study of water clusters using the EFP method and the MD and MC codes. In the first paper, we demonstrated that the EFP method predicts structures and relative energies for water clusters containing three to five water molecules. In a second paper the EFP method is shown to be quite reliable for clusters of up to 20 water molecules, and several alternative Monte Carlo methods are assessed. Related to this work is the study of the effect of water clusters on such important reactions as $\text{S}_\text{N}2$ and Menshutkin.

Although many papers have been written about the simplest amino acid glycine, including the nature of its zwitterion \longleftrightarrow neutral equilibrium, it has proved to be very challenging for theory to correctly predict the energy difference between these two species in solution. We have shown that while the most popular continuum methods are not up to the task by themselves, an approach that combines explicit waters for the first solvation shell with an accurate continuum model is quite successful. The PCM continuum solvation model, including analytic energy gradients, has been interfaced with the EFP method, so that one can efficiently explore the effects of both explicit and bulk solvent. We have now shown that the EFP method, combined with the Monte Carlo/simulated annealing code, does an excellent job of treating problems such as the glycine equilibrium. One paper has been published on this problem and a second paper has been accepted and will appear in print shortly.

Surface Chemistry. The SIMOMM embedded cluster method for studying surface phenomena has recently been applied to several important problems. The first of these illustrated the need to use appropriate wavefunctions when treating the bare reconstructed Si(100) surface. Because there is significant diradical character in the surface dimers, the use of multi-reference wavefunctions is essential. Several papers have been written on this subject, and one more is in preparation. The addition of H₂O (completed) and acetylene and benzene (in progress) to the Si(100) surface have also been studied. In the case of water, the barrier for O-H dissociation is not correctly reproduced unless the bare surface is treated with MCSCF wavefunctions. An extensive study of the oxidation of the Si(100) surface by atomic oxygen has been initiated. This involves the study of the formation of stable surface species (passive oxidation) and the removal of SiO from the surface (active oxidation or etching). Several species on the surface have significant diradical character, so again MCSCF wavefunctions are required. The paper describing this work has received favorable reviews. Related to this surface chemistry is an extensive *ab initio* study of small silicon/carbon clusters. This is an ongoing collaboration with the Lineberger (Colorado) and Burggraf (AFIT) groups. The first study focused on neutral SiC₃ and Si₂C₂ clusters. We are now exploring the corresponding anions, since the experimental groups actually perform photodetachment experiments from these anions.

5. Personnel Supported: List professional personnel (Faculty, Post-Docs, Graduate Students, etc.) supported by and/or associated with the research effort.

Dr. Michael W. Schmidt, Senior Research Associate
Mr. Yuri Alexeev
Dr. Pradipta Bandyopadhyay, postdoctoral research associate
Dr. Brett Bode, graduate student, postdoctoral research associate
Professor Larry Burggraf
Dr. Cheol Ho Choi, postdoctoral research associate
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Mr. Mark Freitag, graduate student.
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Ms. Laura Gregerson, undergraduate student.
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Dr. Grant Merrill, postdoctoral research associate.
Professor Jerzy Moc
Mr. Ryan Olson
Professor Leo Radom, Australian National University.
Ms. Jamie Rintelman, graduate student
Professor Klaus Ruedenberg
Major James Shoemaker

6. Publications: List peer-reviewed publications submitted and/or

accepted during the 12-month period starting the previous 1 October (or since start for new contracts).

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51. A. Yoshikawa, M.S. Gordon, V.F. Sidorkin and V.A. Pestunovich, "Proton Affinity of the Silatranes and Their Analogs", *Organomet.*, 20, 927 (2001).

52. D.G. Fedorov and M.S. Gordon, "Speeding Up Spin-Orbit Calculations", ACS Symposium Series, in press.

53. T. Kudo and M.S. Gordon, "Structures and Stabilities of Titanium Silsesquioxanes", J. Phys. Chem., in press.
54. Y. Alexeev, R.A. Kendall and M.S. Gordon, "The Distributed Data SCF", Computer Physics Commun., **143**, 69 (2002).
55. S. Koseki, Y. Ishihara, H. Umeda, D.G. Fedorov, and M.S. Gordon, "Dissociation Potential Curves of Low-Lying States in Transition Metal Hydrides. I. Hydrides of Group IV", J. Phys. Chem., in press.
56. C.H. Choi, D.-J. Liu, J.W. Evans, and M.S. Gordon, "Passive and Active Oxidation of Si(100) by Atomic Oxygen: A Theoretical Study of Possible Reaction Mechanisms", J. Am. Chem. Soc., submitted.
57. Y. Jung, Y. Akinaga, K.D. Jordan, and M.S. Gordon, "An *ab initio* study of the structure of two-, three- and five-dimer silicon clusters: An approach to the Si(100) surface", Theoret. Chem. Accts., submitted.

7. Interactions/Transitions:

- a. Participation/presentations at meetings, conferences, seminars, etc.

TALKS AT PROFESSIONAL MEETINGS

1. "The Effect of Catalysts on Organosilicon Reaction Mechanisms", National American Chemical Society Meeting, Dallas, TX, April 1998, INVITED.
2. "Gridless Density Functional Theory", presented by K. Glaesemann, ", National American Chemical Society Meeting, Dallas, TX, April 1998.
3. "The Catalyzed Hydrosilation Reaction", presented by B. Bode, ", National American Chemical Society Meeting, Dallas, TX, April 1998.
4. "Theoretical Studies of Explosive Molecules", presented by V. Glezakou, ", National American Chemical Society Meeting, Dallas, TX, April 1998.
5. "Chemical Reaction Dynamics", AFOSR Molecular Dynamics Contractors' Meeting, Monterey, CA, May 1998.
6. "Effect of Solvents on Chemical Processes", Canadian Symposium on Theoretical Chemistry (INVITED), Vancouver, BC, August 1998.
7. "The Role of Theory in Chemical Vapor Deposition", Electrochemical Society

Meeting (INVITED), Boston, November 1998

8. "The Mechanism of Formation of POSS Species", Symposium on High Temperature Materials (INVITED), Maui, HI, January 1999

9. "Effect of the Medium on Chemical Reactions", Morokuma Symposium, Atlanta, GA, May 1999 (INVITED)

10. "Enabling Calculations on Large Molecules Using Parallel Computers", AFOSR High Energy Density Materials Meeting, Cocoa Beach, FL, June 1999 (INVITED)

11. "Medium Effects on Chemical Reactions", American Conference on Theoretical Chemistry, Boulder, CO, June 1999

12. "Restricted High-Spin Open Shell Theory: The Z Average Perturbation Theory (ZAPT) Gradient", presented by Robert Bell, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

13. "Structure and Energetics of Silicon Carbide Clusters, Si_nC_m , $n + m = 4$ ", presented by Jamie Rintelman, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

14. "Improved Implementation of the Fast Multipole Method (FMM)", presented by Cheol Ho Choi, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

15. "Distributed Data MP2 on PC Clusters", presented by Mike Schmidt, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

16. "The Study of Water Solvation of Electrolytes by Using the Effective Fragment Potential Model", presented by Akihiko Yoshikawa, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

17. "A Theoretical Study of the Catalyzed Bis-Silylation Reaction", presented by Yuri Alexeev, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

18. "Full CI and MCSCF Calculations of Spin Density Using Gaussian Basis Sets", presented by Michael Pak, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

19. "Investigation of the First Potential Surfaces of the Systems $\text{B} + \text{H}_2$ and $\text{B}_2 + \text{H}_2$ with Large Scale Ab Initio Calculations", presented by Vassiliki-Alexandra Glezakou, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

20. "QM/MM Methods for solvation and Surface Chemistry", National ACS Meeting, New Orleans, LA, August 1999. (INVITED)

21. "Cycloaddition reactions of 1,3-cyclohexadiene on Silicon (001) surface using SIMOMM", presented by Cheol Ho Choi, National ACS Meeting, New Orleans, LA, August 1999
22. "Direct recurrence relations for the rapid and stable determination of rotation matrices between complex spherical harmonics", presented by Cheol Ho Choi, National ACS Meeting, New Orleans, LA, August 1999
23. "The Effect of the Medium on Chemical Reactions", Royal Australian Chemistry Institute Conference, Canberra, Australia, February 2000 (INVITED).
24. "Silicon Materials and Surface Chemistry", Materials Research Society meeting, San Francisco, April 2000 (INVITED).
25. "Effect of the Medium on Chemical Reactions", Central Regional ACS Meeting, Cincinnati, May 2000 (INVITED)
26. "A Cluster Approach to Solvation and Surface Chemistry", AFOSR Dynamics Contractors' meeting, Boston, May 2000.
27. "Electronic Structure of SiC Clusters, AFOS Dynamics Contractors' meeting, Boston, May 2000, Jamie Rintelman presenting.
28. "Effect of the Medium on Chemical Reactions", Midwest Theoretical Chemistry Conference, Iowa City, May 2000 (INVITED)
29. "Hydrogen Transfer in Materials and Biomolecules", National ACS Meeting, Washington, DC, August 2000 (INVITED)
30. Excited State Potential Energy Surfaces from Diatomics to Biomolecules, National ACS Meeting, San Diego, April 2001 (INVITED)
31. "Effect of Solvation on Chemical Processes", Pacific Basin Chemical Society Meeting, Honolulu, December 2000 (INVITED).
32. "A Cluster Approach to Surface Chemistry", Pacific Basin Chemical Society Meeting, Honolulu, December 2000 (INVITED).
33. "A Cluster Approach to Surface Chemistry", Workshop on Computational Materials Science, Maui, December 2000 (INVITED).
34. "Cluster Approaches to Solvation and Surface Chemistry", New Frontiers in Theoretical Chemistry, Tokyo, March 2001 (INVITED)
35. "The Use of Multi-Reference Wavefunctions in Surface Chemistry", National ACS

Meeting, Chicago, August 2001.

36. "Cluster Approaches to Solvation and Surface Chemistry", National ACS Meeting, Chicago, August 2001.

INVITED LECTURES

1. "Ubiquitous Water", Advanced Supercomputer Center, Wright-Patterson AFB, October 1997
2. "Ubiquitous Water", Coulson Lecture, University of Georgia, October 1997
3. "Ubiquitous Water", University of Utah, November 1997
4. "Ubiquitous Water", Australian National University, January 1998
5. "Ubiquitous Water", Melbourne University, February 1998
6. "Ubiquitous Water", Sydney University, February 1998
7. "Potential Energy Surfaces for Mechanisms in Organometallic Chemistry", University of Iowa, February 1998
8. "Ubiquitous Water", Roseman Lecture, Johns Hopkins University, April 1998
9. "Ubiquitous Water", University of Nebraska, September 1998
10. "The Role of Water in Chemical Processes", Grinnell University, February 1999
11. "Ubiquitous Water", Marquette University, February 1999
12. "The Effective Fragment Method", Pople Symposium, Amelia Island, FL, March 1999
13. "Ubiquitous Water", Long Island University, Brooklyn, NY, March 1999
14. "Water as a Catalyst", Union Carbide Corp., May 1999
15. "The Effect of the Medium on Chemical Reactions", Boston University, October 1999
16. "The Effect of the Medium on Chemical Reactions", University of Arizona, October 1999

17. "The Effect of the Medium on Chemical Reactions", University of Michigan, October 1999
18. "Quantum Chemistry at Iowa State University", University of Sydney, March 2000
19. "Effect of the Medium on Chemical Reactions", Kansas State University, April 2000
20. "Effect of the Medium on Chemical Reactions", Princeton University, May 2000
21. "Cluster Approaches to Solvation and Surface Chemistry", Gustavus Adolphus College, March 2001
22. "Cluster Approaches to Solvation and Surface Chemistry", St. Mary's College, April 2001
23. "Cluster Approaches to Solvation and Surface Chemistry", University of Southern California, April 2001
24. "Cluster Approaches to Solvation and Surface Chemistry", University of California-Irvine, May 2001
25. "Cluster Approaches to Solvation and Surface Chemistry", Australian national University, November 2001
26. "Cluster Approaches to Solvation and Surface Chemistry", Penn State University, February 2002

b. Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories. Provide factual information about the subject matter, institutions, locations, dates, and name(s) of principal individuals involved.

- Served as co-advisor to Major James Shoemaker, who received his Ph.D. from the Department of Engineering Physics, Air Force Institute of Technology, October 1997. Several papers from this work are already in print.
- Collaborating with Dr. Shawn Phillips (AFRL) to determine the mechanisms for the formation of POSS.
- Collaborating with Drs. Paul Day and Ruth Pachter (AFRL) to study the behavior of clusters of water and other solvents.
- Collaborating with Dr. Ruth Pachter to develop density-functional-based effective fragment potentials.

c. Transitions. Describe cases where knowledge resulting from your effort is used, or will be used, in a technology application. Transitions can be to entities in the DOD, other federal agencies, or industry. Briefly list the enabling research, the laboratory or company, and an individual in that organization who made use of your research.

Both GAMESS and MacMolPlt have an increasing number of users in universities, industry, and government laboratories. The latest version of parallel GAMESS is on-line at all DoD Major Shared Resource Centers.

8. New discoveries, inventions, or patent disclosures. (If none, report None.) **None**

9. Honors/Awards: List honors and awards received during the grant/contract period. List lifetime achievement honors such as Nobel prize, honorary doctorates, and society fellowships prior to this effort.

¶ Coulson Lecturer, University of Georgia, October, 1997

¶ Roseman Lecturer, Johns Hopkins University, April, 1998

¶ Named Distinguished Professor of Chemistry, May, 1998

¶ Named to list of 100 most cited chemists, 1981-2000.

10. Markings: In order to ensure prompt receipt and acceptance, mark the outside of the package clearly to indicate that it is a progress report.